



D E C L A R A T I O N

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[TITLE OF DOCUMENT] Specification 1
[TITLE OF DOCUMENT] Drawing 1
[TITLE OF DOCUMENT] Abstract 1
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(Translation)

[DOCUMENT NAME] Specification

[TITLE OF THE INVENTION] LITHIUM ION SECONDARY BATTERY

[CLAIMS]

[Claim 1] A lithium ion secondary battery having: a positive electrode; a negative electrode; an electrolyte comprising a non-aqueous solvent dissolving a lithium salt; and a separator,

wherein said separator is a porous film layer, said porous film layer comprising basic solid particles and a binder, and being adhered to be formed onto said positive electrode or said negative electrode, and

said binder is a composite binder comprising at least a primary binder comprising a heat-resistant resin with higher binding effects, and a secondary binder comprising a flexible resin having excellent binding characteristics with surfaces of said basic solid particles.

[Claim 2] The lithium ion secondary battery in accordance with claim 1, wherein said positive electrode or said negative electrode is a positive electrode of composite oxides or a negative electrode of a carbonaceous material, said primary binder is polyether sulfone, and said secondary binder is polyvinylpyrrolidone.

[Claim 3] The lithium ion secondary battery in accordance with claim 1 or 2, wherein said basic solid

particles are α -alumina.

[Claim 4] The lithium ion secondary battery in accordance with any of claims 1 to 3, wherein the ratio between said basic solid particles and said binder is 96:4 to 99.5:0.5.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to a lithium ion secondary battery, particularly to a preferable separator thereof.

[0002]

[Prior Art]

In chemical batteries such as lithium ion secondary batteries, a separator is provided between positive and negative electrodes in order to electronically insulate the electrodes and further to retain an electrolyte. Currently, in lithium ion secondary batteries, a microporous thin film mainly comprising polyethylene is used.

As a means to enhance high rate and cycle life characteristics, proposed has been a structure in which a porous film layer is formed on at any one of or both of positive and negative electrodes, instead of a conventional structure, that is, a resin sheet separator is disposed between positive and negative electrodes. (For example, see patent document 1)
This structure enabled simplification of a lithium ion

secondary battery which further needed a separator, making its formation easier. Also, this structure has an effect to suppress defects of short circuits based on misalignment of a separator, which is another structural component.

[0003]

[Patent Document 1]

Japanese Laid-Open Patent Publications No. Hei 10-106530

(claim 15, FIG.2)

[0004]

[Problem That the Invention Is to Solve]

Nevertheless, based on insufficient adhesiveness of polymer binders, an addition of at least 5% of the polymer binder was necessary in order to adhere the porous film layer to the electrode, and therefore, flexibility is lost to cause some problems in that resin deterioration greatly affects a battery life, and high rate characteristics decline.

[0005]

The present invention aims to solve the above problems, and to provide a lithium ion secondary battery having a porous film layer with superior characteristics of both adherence and flexibility even with a small amount of a binder and having superior high rate and cycle life characteristics.

[0006]

[Means for Solving the Problem]

In order to solve the above problems, in the present invention, a lithium ion secondary battery having positive and

negative electrodes, an electrolyte in which a lithium salt is dissolved in a non-aqueous solvent, and a separator is characterized in that the separator is a porous film layer comprising basic solid particles and a binder, and being adhered to be formed onto the positive electrode or the negative electrode; and the binder is a composite binder comprising at least a primary binder comprising a heat-resistant resin with higher binding effects, and a secondary binder comprising a flexible resin having excellent binding characteristics with surfaces of the basic solid particles.

[0007]

Herein, the primary binder is a heat resistant and flame-retardant resin with excellent binding effects between resins and with excellent dimensional stability. Such resin has excellent binding effects, but when used alone, its binding characteristics with surfaces of basic solid particles are poor. Secondary binder comprising a flexible resin having excellent binding characteristics with surfaces of basic solid particles has effects to complement such resin.

[0008]

Further, the above effects are obtained to the maximum and it is preferable when the positive electrode or the negative electrode is a positive electrode of composite oxides or a negative electrode of a carbonaceous material; the primary binder is polyether sulfone(PES); and the secondary binder is polyvinylpyrrolidone(PVP).

[0009]

Also, as a result of diligent study of inventors, it was revealed that basic solid particles have effects of a high-speed diffusion of lithium ion, compared with acidic particles such as silica. Although no details are known regarding such effects, it is probably related with reactivity of lithium ion at surfaces of the basic solid particles. Herein, the amount of resin can be made smaller by using a composite binder and surface properties of the basic solid particles can be effectively utilized. An improvement in high rate characteristics in lithium ion secondary batteries can be expected due to the improvement of the diffusion speed.

[0010]

Further, the above effects are obtained to the maximum and it is preferable when the basic solid particles are α -alumina. And it is preferable that the ratio between the basic solid particles and the binder is 96:4 to 99.5:0.5.

[0011]

[Mode for Embodying the Invention]

The present invention intends to provide: a separator which is a porous film layer comprising basic solid particles and a binder, the separator being adhered to be formed onto a positive electrode or a negative electrode; and a composite binder comprising at least a primary binder comprising a heat-resistant resin with higher binding effects, and a secondary

binder comprising a flexible resin having excellent binding characteristics with surfaces of the basic solid particles.

[0012]

Misalignment and gaps are hardly created even when a greater degree of mechanical stresses are applied due to a battery structure of winding, laminating, and the like, since the porous film layer is adhered to be formed onto the positive electrode or the negative electrode. Since the negative electrode usually has a larger dimension than the positive electrode in lithium ion secondary batteries, it is preferred that the porous film layer is formed on a surface of the negative electrode.

[0013]

Any conventionally known positive electrode is used as the positive electrode of the present invention, but it is preferred that a composite oxide such as lithium cobaltate, and lithium nickelate is used as the active material. The positive electrode is produced by preparing a material mixture containing an active material of such composite oxide, a conductive material, and a resin binder, and then applying the prepared mixture onto both faces of a current collector.

[0014]

Any conventionally known negative electrode is used as the negative electrode of the present invention, but it is preferred that the negative electrode uses a carbonaceous material such as artificial graphite and natural

graphite as an active material. The negative electrode is produced by preparing a material mixture containing a carbonaceous material, conductive agent, and a binder, and then applying the mixture onto both faces of a current collector.

[0015]

The binder is characterized in that it is a composite binder, comprising at least a primary binder comprising a heat-resistant resin with higher binding effects, and a secondary binder comprising a flexible resin having excellent binding characteristics with surfaces of the basic solid particles.

[0016]

Herein, the primary binder is a heat-resistant and flame-retardant resin with higher binding effects between resins and with dimensional stability, such as polymers comprising polyether including sulfur. Among these polymers, PES is preferable, since it has self-extinguishing characteristics and is stable under a high potential in a battery. For the secondary binder comprising a flexible resin having excellent binding characteristics with the surfaces of basic solid particles, polymers comprising polyvinyl including nitrogen can be mentioned. Among these polymers, PVP is preferable, since it has excellent binding characteristics with basic solid particles, especially with surfaces of α -alumina; has good affinity with polyether such as PES; and has

flexibility.

[0017]

For the basic solid particles of the present invention, basic ceramic materials such as magnesium oxide can be mentioned. Among them, particularly preferred is α -alumina.

[0018]

As to the ratio between basic solid particles and the binder, when an amount of the binder is large, the surfaces of the basic solid particles are covered with the binder, reducing the effects of the present invention. Conversely, when an amount of the binder is small, the strength of the porous film layer decrease. Therefore, the preferable range is 96:4 to 99.5:0.5.

[0019]

[Working Examples]

Next, the specific examples of present invention are described based on EXAMPLEs.

[0020]

A cylindrical battery described below is manufactured, in order to evaluate high rate characteristics and cycle life characteristics of a battery of the present invention.

(EXAMPLE 1)

A positive electrode was made by mixing 85 wt% of powdered lithium cobalt oxide, 10 wt% of powdered carbon as a conductive material, and 5 wt% of polyvinylidene fluoride (PVdF resin) as a binder; preparing a slurry by dispersing

the mixed material in dehydrated NMP; applying the slurry onto a positive electrode current collector made of aluminum foil, drying the slurry; and then rolling.

[0021]

For a negative electrode, artificial graphite powders were used as a negative electrode active material. The negative electrode was made by mixing 95 wt% of artificial graphite powder and 5 wt% of PVdF resin as a binder; preparing a slurry by dispersing the mixture in dehydrated NMP; applying the slurry onto a negative electrode current collector made of copper foil; drying the slurry; and then rolling.

[0022]

A mixture of 100 grams in total was stirred and mixed for 30 minutes by a mixer (Rentaro MX201 available from Thinky Corporation), with the compositional proportion of the mixture of 96 parts by weight of α -alumina (AKP50 manufactured by Sumitomo Chemical Co., Ltd.), 1.6 parts by weight of PES (Sumikaexcel PES5003P manufactured by Sumitomo Chemical Co.), 2.4 parts by weight of PVP (LUVITEC-K90 manufactured by BASF Japan Ltd.), and 100 parts by weight of NMP (normal methylpyrrolidone) as a solvent. The paste was applied onto the negative electrode by a comma roll coater to give a film thickness of 20 μm . Subsequently, the applied paste was dried with a hot blast of 100°C for about 15 minutes. Such sequence of processes was conducted for both faces of the negative electrode, to obtain a film-formed negative electrode.

[0023]

As this film-formed negative electrode was observed with a scanning electron microscope (SEM), it was confirmed that layers with a structure in which solid particles were layered were made, as shown in FIGs. 1 and 2.

[0024]

This was combined with the positive electrode. An electrolyte was charged and sealing was conducted to make a battery. Herein, for the electrolyte, to a mixed solvent of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) with a volume ratio of 1:1, LiPF_6 was dissolved at 1 mol/liter. The amount of the electrolyte was about 3.8 ml.

[0025]

The cylindrical battery thus made had a diameter of 18 mm and a height of 65 mm. The designed capacity of the batteries in EXAMPLEs was set as 2000 mAh.

[0026]

(EXAMPLE 2)

A battery was assembled in the same manner as in EXAMPLE 1 except that the composition ratio of the following was used: 99.5 parts by weight of α -alumina, 0.1 part by weight of PES, 0.4 part by weight of PVP, and 100 parts by weight of NMP (normal methylpyrrolidone) as a solvent.

[0027]

(COMPARATIVE EXAMPLE 1)

A battery was assembled in the same manner as in

EXAMPLE 1 except that no porous film layer was formed on the electrode and a conventional polyethylene separator with a thickness of 25 μm was used.

[0028]

(COMPARATIVE EXAMPLE 2)

A battery was assembled in the same manner as in EXAMPLE 1 except that the following composition ratio was used: 95 parts by weight of α -alumina, 2 parts by weight of PES, 3 parts by weight of PVP, and 100 parts by weight of NMP (normal methylpyrrolidone) as a solvent.

[0029]

(COMPARATIVE EXAMPLE 3)

When only PES was used as the resin material, although an attempt was made to fabricate a battery in the same manner as in EXAMPLE 1, a hard film was made and flexibility was not obtained, failing to wind the battery.

[0030]

(COMPARATIVE EXAMPLE 4)

When only PVP was used as the resin material, although an attempt was made to fabricate a battery in the same manner as in EXAMPLE 1, the film became weak and peeled off, being unable to maintain the structure.

[0031]

(COMPARATIVE EXAMPLE 5)

When only PVdF was used as the resin material, although an attempt was made to fabricate a battery in the

same manner as in EXAMPLE 1, the film became weak and peeled off, being unable to maintain the structure.

[0032]

[Battery Evaluation]

For the batteries of EXAMPLES 1 and 2, and COMPARATIVE EXAMPLES 1 and 2, which were able to be fabricated, the evaluations below were conducted.

[0033]

The designed capacity of the batteries was 2000 mA. The batteries were charged with a constant current of 2000 mA(1C) until reaching 4.2 V, first, and afterwards, the batteries were charged with a constant current of 4.2 V until reaching 100 mA(0.5C). Further, the batteries were discharged with a constant current of 1C until reaching 2.5 V. A cycle of charge and discharge was carried out 10 times. The discharge capacity at the 10th cycle was set as the initial capacity of each battery. In all 4 batteries, the initial capacity satisfied the design capacity. The charge and discharge were carried out in a constant temperature bath of 20 °C.

[0034]

Then, after each battery was charged with a constant current of 1c) until reaching 4.2 V, each battery was charged with a constant current of 4.2 V until reaching 0.05C, and discharged with 400 mA (0.2C) until reaching 2.5 V. This capacity was set as 0.2C capacity. Further, the same charge,

and discharge with each rate of 1C, 2C, 3C, 4C, and 5C were carried out. High rate characteristics were evaluated. The results are summarized in (Table 1), showing capacity variations setting 0.2C capacity as 100%.

[0035]

[Table 1]

Charge/Discharge Rate (C)	Capacity Variations (%)			
	Ex. 1	Ex. 2	Comp. Ex. 1	Comp. Ex. 2
0.2	100	100	100	100
1	99.5	99.7	98.6	99.1
2	98.9	99.1	97.4	97.9
3	95.4	95.7	89.1	89.4
4	90.2	91.4	79.5	81.1
5	84.3	86.1	69.3	71.3

[0036]

Then, a cycle of charging until 4.2 V with 1C and discharging until 2.5 V with 1C was carried out to measure a capacity retention rate setting the initial capacity as 100%. The results are summarized in (Table 2).

[0037]

[Table 2]

Cycle Number	Capacity Retention Rate (%)			
	Ex. 1	Ex. 2	Comp. Ex. 1	Comp. Ex. 1
0	100	100	100	100
50	101.3	101.7	99.1	99.3
100	99.7	100.3	98.4	98.9
200	99.2	99.6	94.6	95.3
300	98.9	99.4	88.4	89.9
500	93.8	95.2	80.2	83.4
750	89.1	92.6	76.4	78.7
1000	83.6	85.4	65.3	68.1

[0038]

As is clear from Tables 1 and 2, the batteries of EXAMPLES 1 and 2, which were the batteries of the present invention, were superior in both high rate and cycle life characteristics compared with the battery of COMPARATIVE EXAMPLES 1 and 2.

[0039]

Besides, in the method of the present invention, it is not necessary to make separators porous as in conventional separator film or resin layer with separator functions. The effects of improved product stability were thus obtained because the process for battery production was simplified and no management for porous-making was necessary.

[0040]

[Effects of the Invention]

As stated above, according to the present invention, a lithium ion secondary battery excellent in high rate characteristics and cycle life characteristics can be provided, since porous film layer can be easily formed into an electrode plate shape for the usage in a battery.

[BRIEF EXPLANATION OF THE DRAWINGS]

[FIG.1]

An SEM image showing a cross-section of a porous film layer made in an example of the present invention.

[FIG.2]

An enlarged SEM image of FIG. 1.

Hei 2003-044552

(Translation)

[DOCUMENT NAME] Abstract

[ABSTRACT]

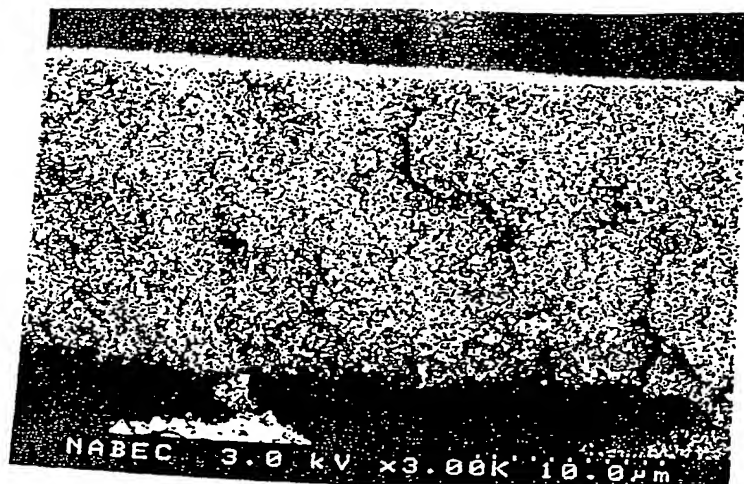
[OBJECTIVE] To provide a lithium ion secondary battery excellent in high rate characteristics and cycle life characteristics, the lithium ion secondary battery having a porous film layer excellent both in binding characteristics and flexibility with a usage of a small amount of binder.

[SOLVING MEANS] A lithium ion secondary battery comprising: a positive electrode, a negative electrode, an electrolyte prepared by dissolving a lithium salt in a non-aqueous solvent, and a separator, wherein the separator comprises a porous film layer containing basic solid particles and a binder, the porous film being adhered to be formed onto the positive electrode or the negative electrode; the binder comprises a primary binder comprising a heat-resistant resin with high binding effects and a secondary binder comprising flexible resin having excellent binding characteristics with surfaces of the basic solid particles.

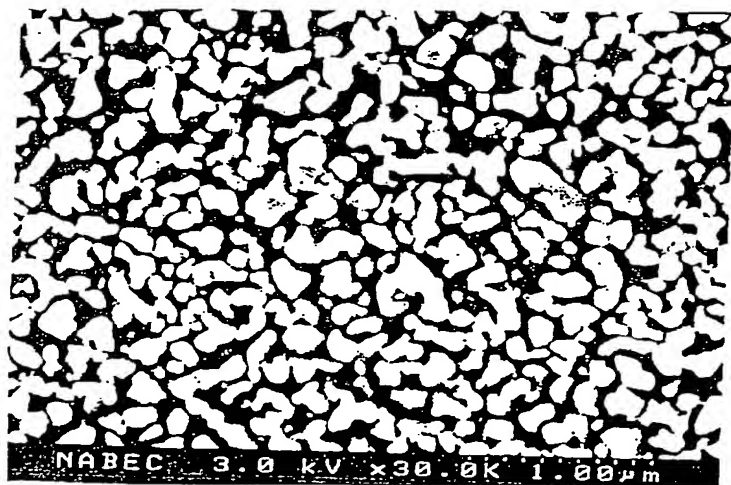
[SELECTED DRAWING] FIG. 2

【書類名】 図面 [DOCUMENT NAME] Drawings

【図 1】 [FIG. 1]



【図 2】 [FIG. 2]



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